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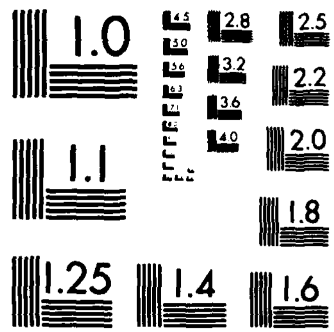
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THE USE OF MICRODIELECTROMETRY IN MONITORING THE CURE OF CARBON-EPOXY PREPREG

Z. N. Sanjana
Principal Investigator

Technical Report No. 3 - Final

SEPTEMBER
~~August~~ 1986

Department of the Navy
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Contract No. N00014-82-C-0164

Westinghouse R&D Center
1310 Beulah Road
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Block 20 (Abstract)

As thermosetting resins and composites made from them begin to be used in critical applications, it becomes necessary to monitor and analyze the cure of the resin within the confines of the processing equipment. Such measurements have been carried out using a dielectric technique called dielectrometry or dielectric analysis. Conventional dielectrometry has certain limitations associated with the use of parallel plate geometry for electrodes. For in situ measurement of cure, intrusiveness of electrodes is a problem which may require placement of electrodes in non-strategic areas. Since electrode spacing changes during cure, it is difficult to deduce permittivity and loss factor from the data. At lower frequencies the capacitive currents are small and signal-to-noise ratios are small, therefore, measurement at low frequencies (<100 Hz) typically require large electrode sizes.

One approach to overcome the problems described above is the development of microdielectrometry. A solid state integrated circuit chip, 2 mm x 4 mm in size, is used as the sensor. The miniature sensor can measure the properties of a dielectric on its surface, therefore it need not intrude into the composite part. Transistors which are built into the integrated circuit are used to amplify the signal to make low frequency (<1 Hz) measurements feasible. The electrode geometry does not change, therefore loss factor and permittivity data can be deduced in real-time. During cure of the resin or composite material, permittivity and loss factor are measured continuously at a series of preselected frequencies. Real-time data is plotted on a strip chart and is also stored in a cassette for later analysis. Temperature of the curing material is measured either by a diode on the sensor or by externally placed thermocouples.

Results on commercially available carbon-epoxy prepregs are presented in this report. Results show that microdielectrometry can be used to follow the cure of the prepreg and absolute measurements of permittivity and loss factor can be made to provide information on the mechanisms that produce the observed changes. Data at <1 Hz can be obtained. For these systems prior to gelation at typical cure temperatures, the data is often out of range of the instrument, requiring the use of a high conductivity option (which we do not have) for monitoring that regime of cure. Lower than expected permittivity values at the end of cure indicate some problems with resin separation from the chip surface. Experiments with aged prepregs are also described.

FOREWORD

The following final report describes part of the work performed under ONR Contract No. N00014-82-C-0164, "Monitor Cure of Composites and Evaluate Cure Monitoring Procedures". The report (Final Report No. 3) covers the work done with Micromet System II and a flat ribbon sensor which permits working with composites. Previous reports dealt with using System I instrumentation on resins (Report No. 1) and prepreg (Report No. 2).

This program was administered for ONR by Dr. L. H. Peebles, Jr. The program was conducted entirely at the Westinghouse Electric Corp., R&D Center, in the Polymer and Composite Research Department with Z. N. Sanjana as Principal Investigator.

THE USE OF MICRODIELECTROMETRY IN MONITORING THE CURE OF CARBON-EPOXY PREPREG

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1. INTRODUCTION

As thermosetting resins and advanced composites made from them begin to be used in critical applications it becomes necessary to monitor the cure of the thermosetting resins within the confines of the processing equipment. Such measurements of cure have been carried out by several investigators using a dielectric technique generally called dielectric analysis.[1-6] In conventional dielectric analysis the sample to be examined is placed between two parallel conducting plates or electrodes and the ac capacitance and dissipation factor are measured using a device called an automatic dielectrometer. One such automatic dielectrometer, popularly called by its acronym Audrey, has been frequently used. It provides a continuous output of dissipation factor and capacitance as a function of time, temperature and frequency (from 0.1 kHz to 100 kHz). It has been successfully used in studying parameters affecting cure[1-3], in situ monitoring of cure in an autoclave[4], and features of the dielectric output have been related to changes in chemistry[5].

There are certain problems associated with conventional dielectrometry, main'y centered around the use of the parallel plate geometry for electrodes. For in situ measurement of cure the placement and intrusiveness of the electrodes becomes an issue. Also, since parallel plate spacing can change during cure, it is difficult to deduce from the capacitance and dissipation factor curves the fundamental dielectric properties, permittivity and loss factor. The use of conductive fibers such as graphite and boron require special treatment of the sample space which at low frequencies become very small and therefore signal-to-noise ratios become small.

Microdielectrometry(6,7) is a technique developed as one approach to overcome some of the problems described above. Integrated circuit technology is used to develop a miniaturized probe that combines a small size with built-in amplification to measure dielectric properties of polymers at frequencies as low as 0.1 Hz. The integrated circuit device consists of a planar interdigitated electrode structure with a pair of matched field effect transistors. The electrode geometry does not change during cure and is reproducible from device to device.

Figure 1 shows the conceptual difference between parallel plate dielectrometry and microdielectrometry.

2. EXPERIMENTAL

Our System I Microdielectrometer was modified to System II specifications by Micromet Instruments, Inc.[8] It is shown schematically in Figure 2. The major change was the use of a Fourier transform analyzer which permits acquisition of very low frequency noise-free signals. The system, in essence, takes the relative gain and phase of the sensor output compared to sensor input (imposed sinusoidal voltage under command from a programmed computer) and using an internally stored calibration converts the data into permittivity (ϵ'), loss factor (ϵ'') and their ratio the loss tangent or dissipation factor ($\tan \delta = \epsilon''/\epsilon'$). Thus ϵ' and ϵ'' can be measured for any material that is on the surface of the integrated circuit chip or sensor. The sensor consists of a 2 mm x 4 mm integrated circuit mounted in a flat cable package shown in Figure 3. Both electrodes used in the dielectric measurement are placed on the same surface to form an interdigitated capacitor and on-chip amplification produces high signal-to-noise ratios.[7]

Our previous measurements of the cure of epoxy resins were made by placing a drop of the curing mixture on the sensor surface. Here, 200 gm quantities of resin were placed in a pan, the sensor was immersed in the resin and cure was carried out in an oven. The flat ribbon cable connects the sensor to the sensor interface box as shown schematically in Figure 2. The oven temperature was either ramped or controlled at a set temperature by means of a controller.

1.1 Materials and Cure Schedule

The resin reported on here is Hercules 3501-6 which was kept frozen at -20°C until ready for use. The resin is a proprietary composition whose principal constituents are a tetrafunctional resin and tetraglycidyl methylene dianiline, cured with diaminodiphenyl sulfone.

Unidirectional carbon prepreg consisting of AS-4 fiber impregnated at 42% resin content with the 3501-6 resin was obtained from Hercules, Inc. Laminates were made from a 40 ply, 0-90 symmetric lay-up. Prepreg cure was studied and compared to that of the resin. The resin was cured in a programmable oven; the prepreg was cured in a programmable press. An identical cure cycle was used for both and is typical of the cure used for this prepreg. It is as follows:

1. At a rate of 4°F raise temperature to 240°F (116°C).
2. Hold at 240°F for 70 mins.
3. At a rate of 4°F raise temperature to 350°F (177°C).
4. Hold at 350°F for 130 mins.
5. Cool.

Post-cure: 4 hrs @ 350°F.

For the prepreg cure a pressure of 50 psi (345 kPa) was used throughout the cure cycle.

Temperatures were measured using both a calibrated thermocouple and the temperature measuring on-chip diode. In general the agreement between the two was fairly good with the diode indicating a temperature a few degrees (5-10°F) higher than the thermocouple. This is shown in Figures 4 and 5. The temperature data presented in this report uses the output of the thermocouple.

1.2 Sensor Location For Prepreg Cure

In order to avoid electrode contact with conducting carbon fibers, the sensor active surface was always separated from the prepreg by either a small piece of glass fabric or by porous PTFE coated glass release sheet. Three sensor locations were tried: (a) sensor was placed in a channel cut in the bottom tooling plate, (b) a channel was cut in the middle 4 plies of prepreg and the sensor was located there, and (c) sensor was placed active face down on top of the porous PTFE coated glass release cloth and channels were cut in the bleeder plies to accommodate the sensor,. In (a) and (b) a small piece of glass fabric was used on top of the sensor; in (c) that was not necessary.

In general all three locations provided meaningful results about the state of cure and post-cure but no location was immune from a nagging problem - the resin either only partially wetted the surface or partially separated from the surface at some point in cure after gelation. The chief evidence of this was that final cured permittivities were much less than the anticipated 4.0. Sometimes the cured permittivities were less than 2.0.

3. RESULTS AND DISCUSSION

3.1 Resin

Figures 6 and 7 present the loss factor and permittivity data on a 200 gm casting of the resin. The large exotherm peak in the temperature is noted when the oven temperature approaches 350°F. Prior to gelation, which generally occurs 30 mins after reaching final cure temperature of 350°F (for this resin and this particular cure schedule) large amounts of the data are lost by virtue of being "off-scale". The fully cured permittivity is about 4.00 (Figure 7) and the low frequency loss factor data shows a continuing reduction in magnitude indicating continuing reaction after 4 hrs at 350°F. The low frequency (0.1 Hz, 1.0 Hz, 10 Hz) loss factor data is dominated by conductivity as indicated by the inverse relationship with frequency (i.e., $\epsilon'' \alpha 1/f$). Higher frequencies do not show this presumably because of dipolar effects.

3.2 Prepreg Cure

3.2.1 Sensor Placed in Channel Cut in Bottom Tooling Plate

Figures 8 and 9 present loss factor and permittivity data for the cure of prepreg for the sensor located as shown in Figure 3. As in the resin cure, the loss factor data prior to gelation are largely "off-scale". This indicates a clear need for the ability to measure high conductivities in the early stages of cure. Instrumentation for such measurements is now available from Micromet Instruments.[8] After gelation (about 30 mins after 350°F is achieved) the loss factor drops rapidly but continues to show reductions indicating continuing cure throughout the cure cycle. As in the case of neat resin the data at the lower frequencies is conductivity dominated; this also shows up in the low frequency permittivity data at the end of cure due to formation of a charged "blocking-layer".[9] The high frequency permittivity data is well behaved and is around 4 at the end of cure. In Figures 8 and 9 the formation of a dispersion region and dipolar peaks is noted as the laminate is cooled down. The post-cure data of Figure 10 shows continuing reaction and a consequent reduction in conductivity and loss factor throughout the post-cure.

3.2.2 Sensor Placed on Top of Release Sheet

Figures 11-13 show the data with the sensor chip turned face down on top of the porous PTFE coated glass release sheet. Such a location is probably optimum because it does not intrude into the laminate nor does it require cutting the tooling. The data are essentially identical to the measurements shown in Figures 8-10.

Sensors located within the body of the laminate also showed results identical to those shown in Figures 8-13. Regardless of sensor location, many of the runs had lower than realistic final permittivity values ($\simeq 4$). It is hypothesized that this was due to poor wetting of the sensor active surface and a subsequent shrinking away of the resin from some portions of the active surface. Within the scope of this program it has not been possible to define when or how this happens or how to prevent it from taking place. It may not be a problem with other resin systems[10] and may not occur in an autoclave cycle in which vacuum is pulled on the prepreg reducing voids due to volatiles, or with high pressure cures when cloth is used.

3.2.3 Prepreg Aging

It is reasonable to expect that as the prepreg is aged (advanced) it will begin to flow onto the sensor surface at higher temperatures and the loss factor values, which are inversely proportional to viscosity, will be lower at any given temperature. That this does occur is clearly shown in Figures 14-16 where during the initial heatup the loss factor is plotted as a function of temperature for prepreg which has been progressively advanced by heat and humidity. The three day data was rerun to show duplication.

4. CONCLUSIONS

Microdielectrometry can be successfully used to follow the cure of resins and carbon-epoxy prepregs indicating, viscosity changes, the region of gelation and the effectiveness of additional cure or post-cure. Pregelation conductivity of typical useful epoxy resins is such that it requires the use of a high conductivity sensor if pregelation data over large frequency ranges is to be obtained.

Aging of prepreg can be monitored by measuring the loss factor data as a function of temperature during the initial heatup of the prepreg. As the prepreg is aged or advanced, the loss factor measurements at a fixed temperature are lower.

5. ACKNOWLEDGMENT

The advice of Dr. D. Day of Micromet Instruments, Inc., and of Prof. S. Senturia of MIT are gratefully acknowledged.

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J. D. B. Smith, Manager
Polymer & Composite Research

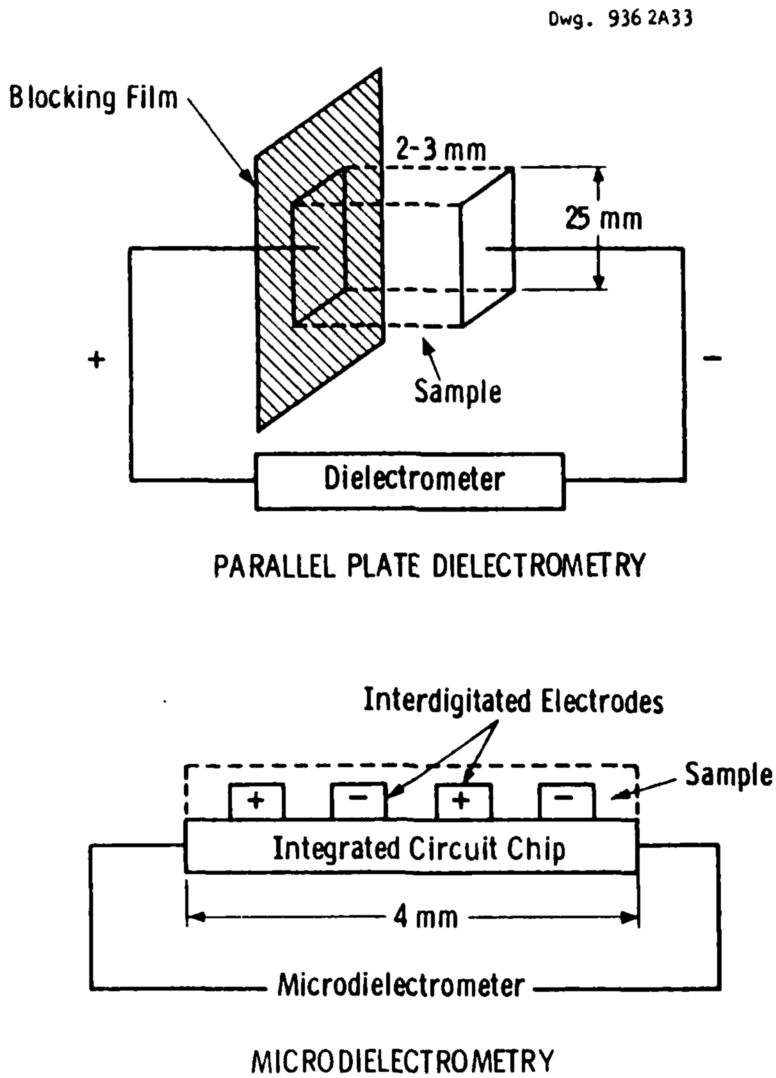

Fig. 1—Schematic differences between conventional dielectrometry and microdielectrometry. Not drawn to scale

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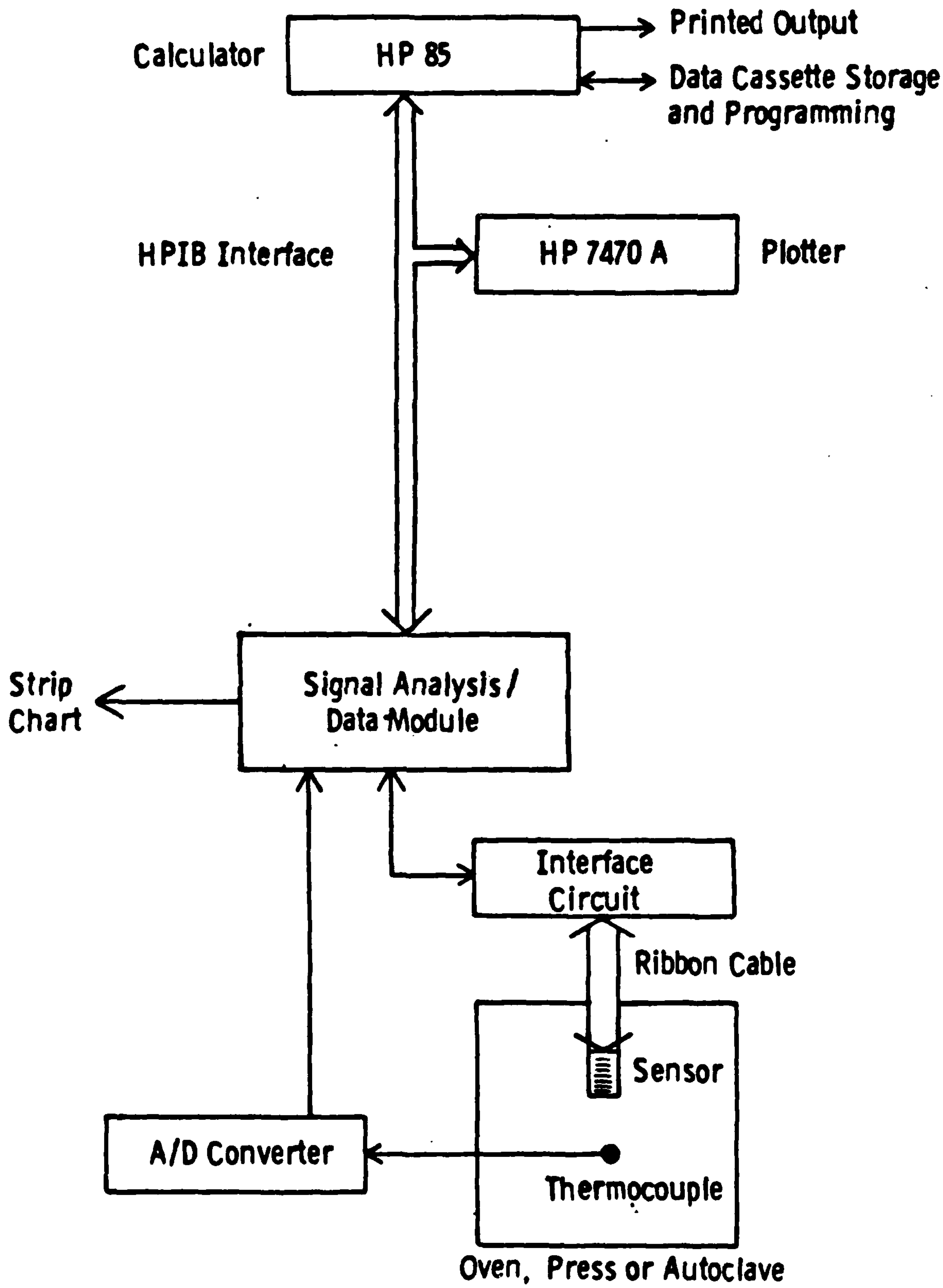


Fig. 2 — Block diagram of measuring system for microdielectrometry

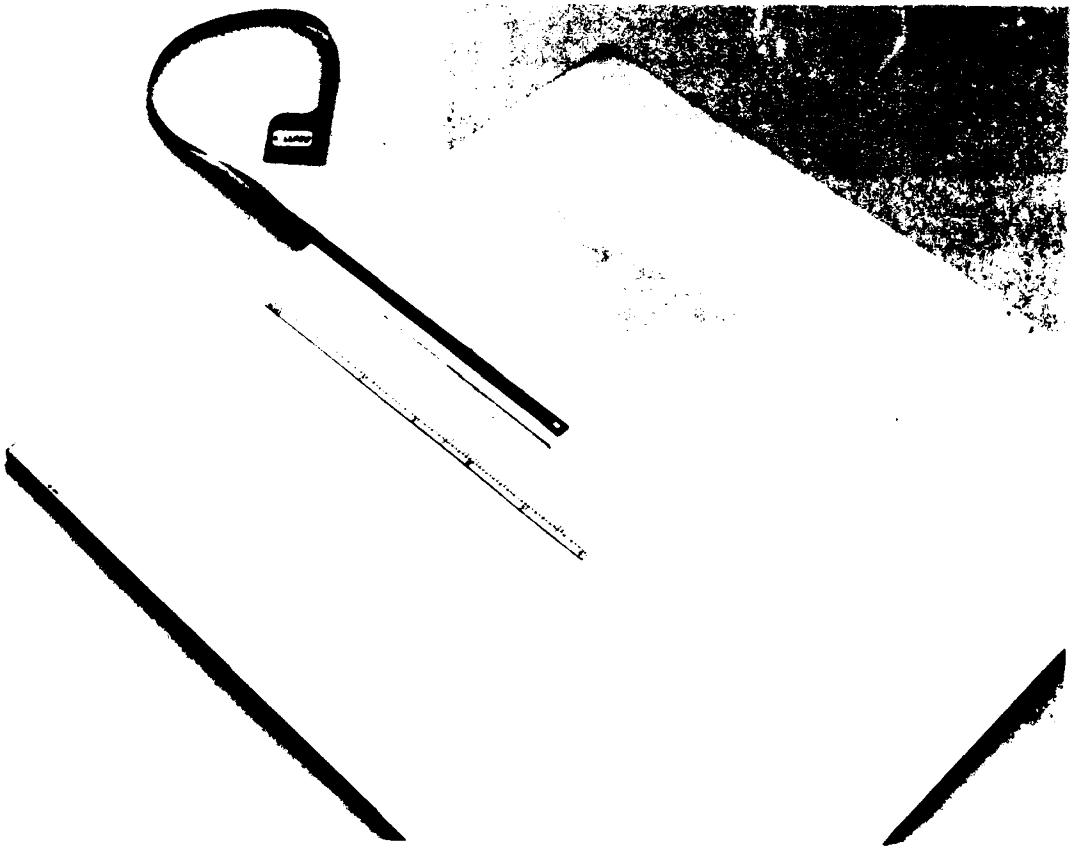
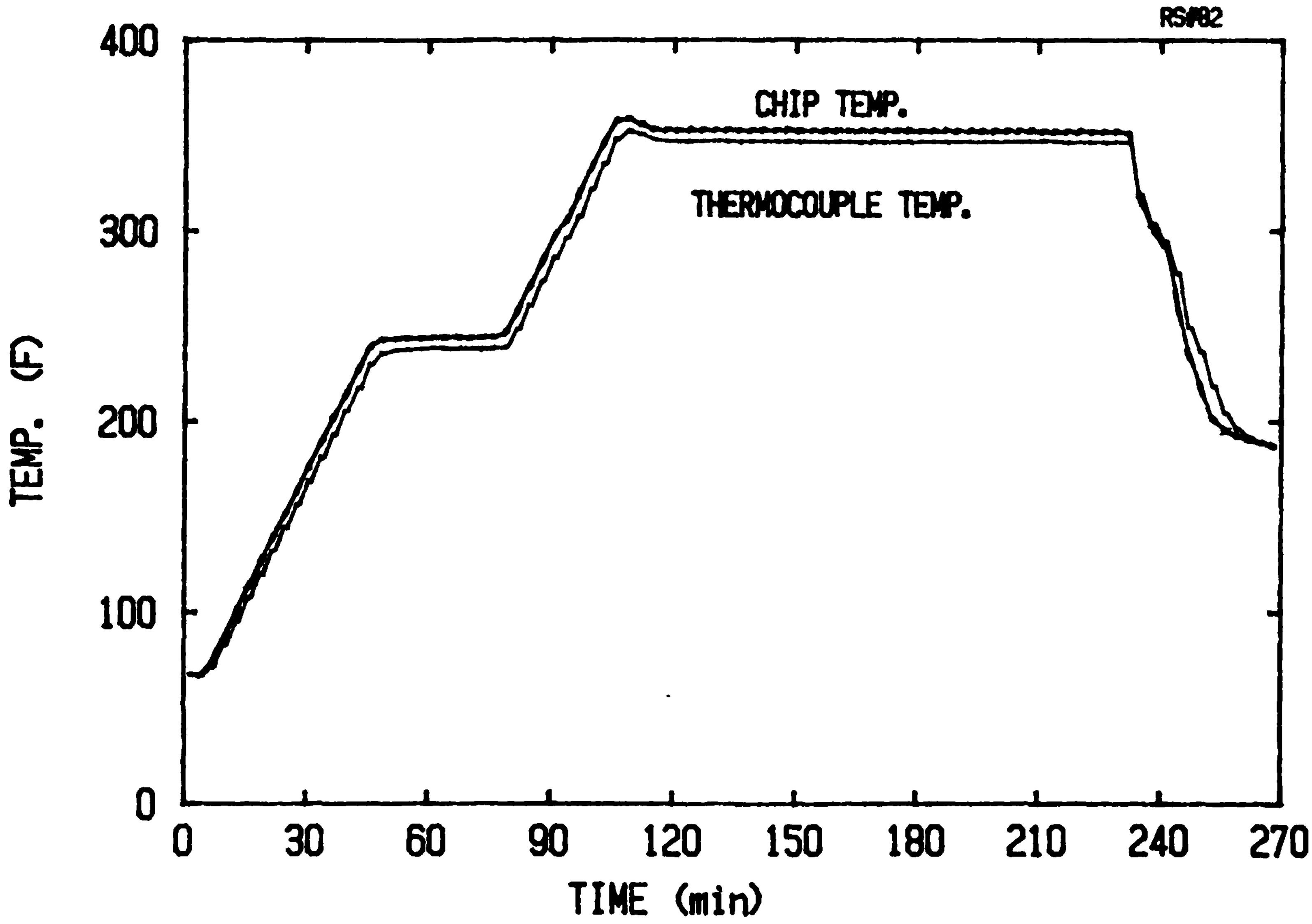


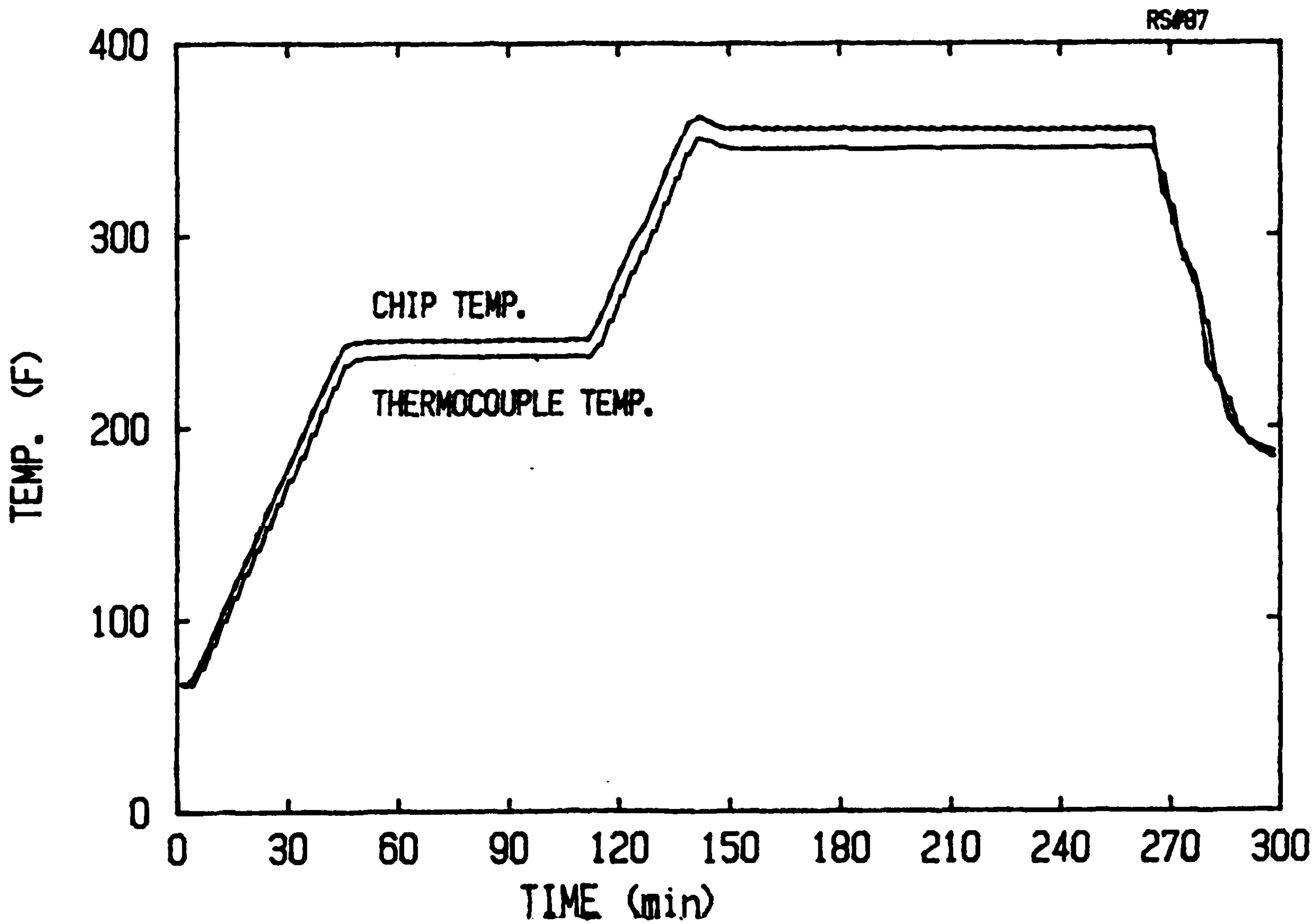
Figure 3 -- Sensor packaged in a flat ribbon connector. Channel cut in platen to accommodate sensor and connector.

FIGURE 4



CURE OF 3501-6/AS4 CARBON EPOXY PREPREG IN PRESS
CHIP TEMPERATURE VS THERMOCOUPLE TEMPERATURE

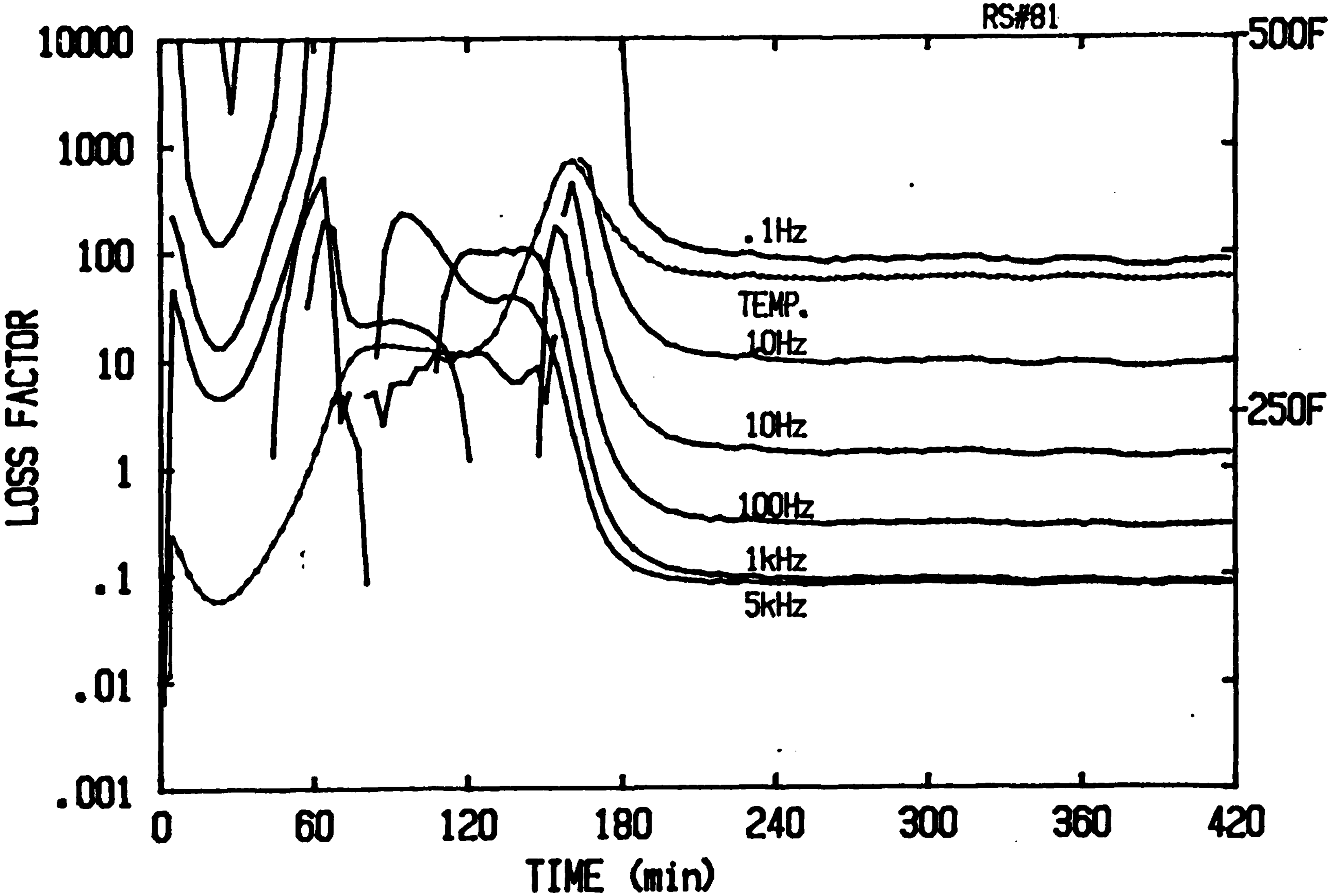
FIGURE 5



CURE OF 3501-6/AS4 CARBON/EPOXY PREPREG IN PRESS

CHIP TEMPERATURE VS THERMOCOUPLE TEMPERATURE

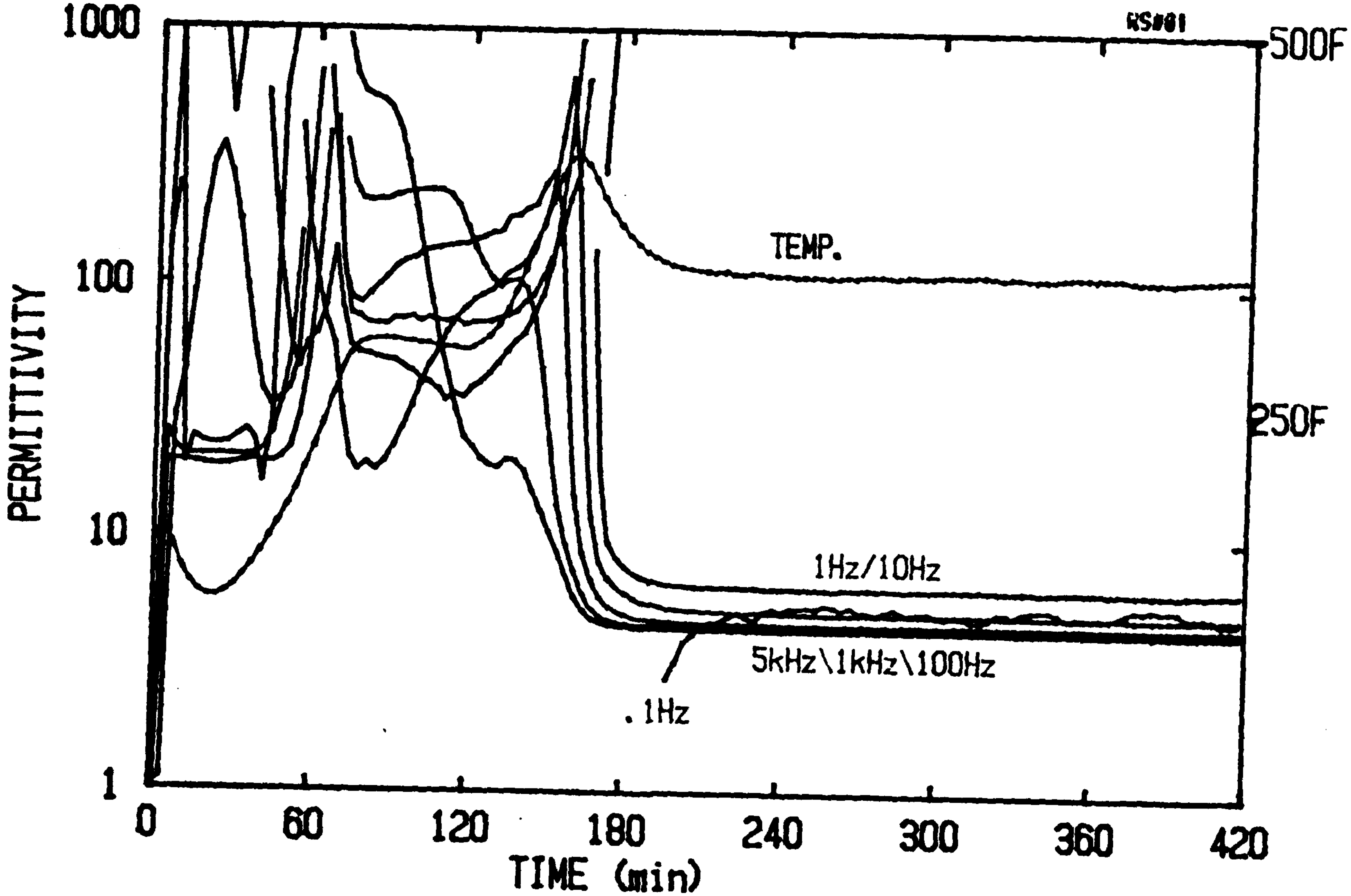
FIGURE 6



CURE OF 3501-6 RESIN IN OVEN

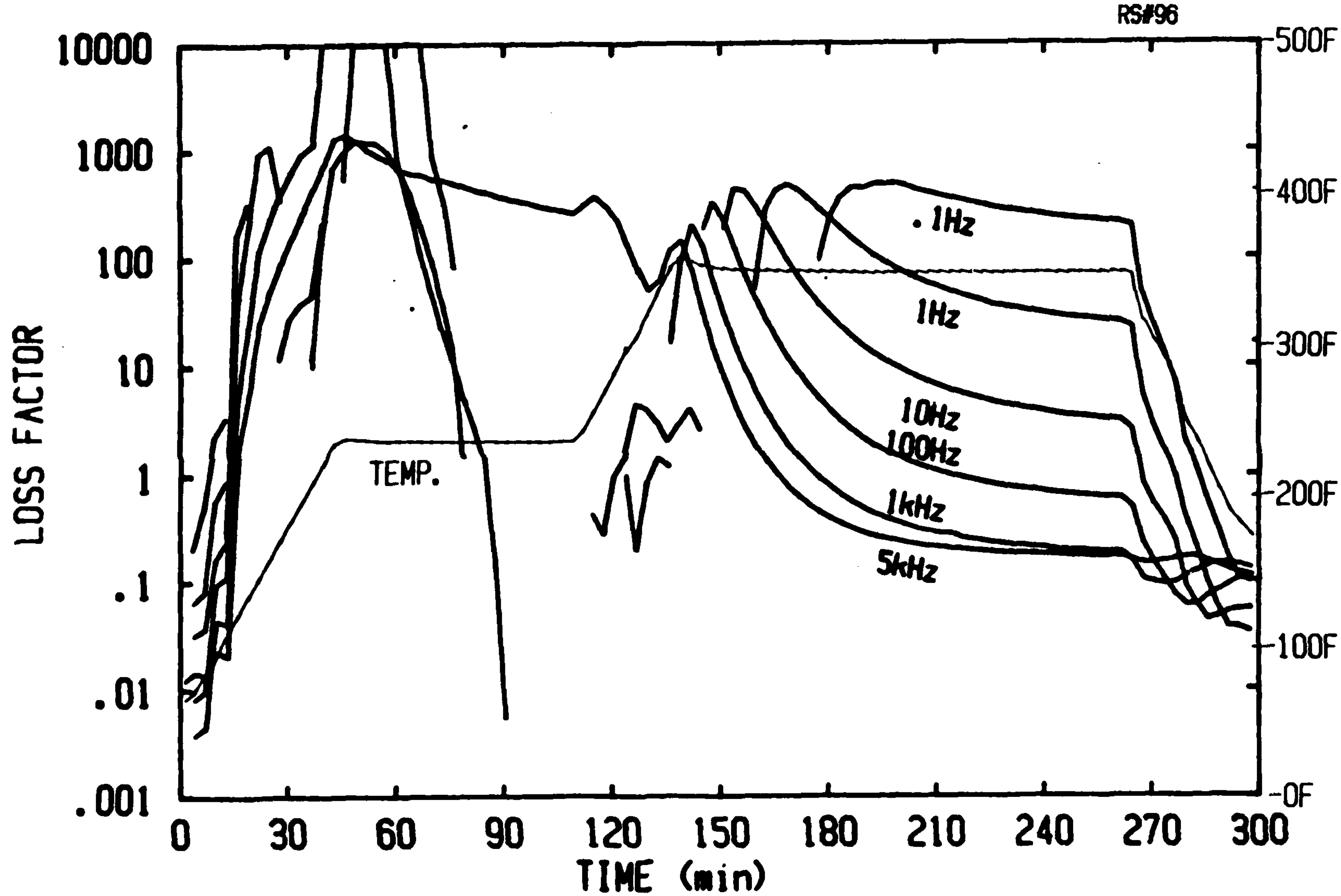
AUTOCLAVE CURE CYCLE

FIGURE 7



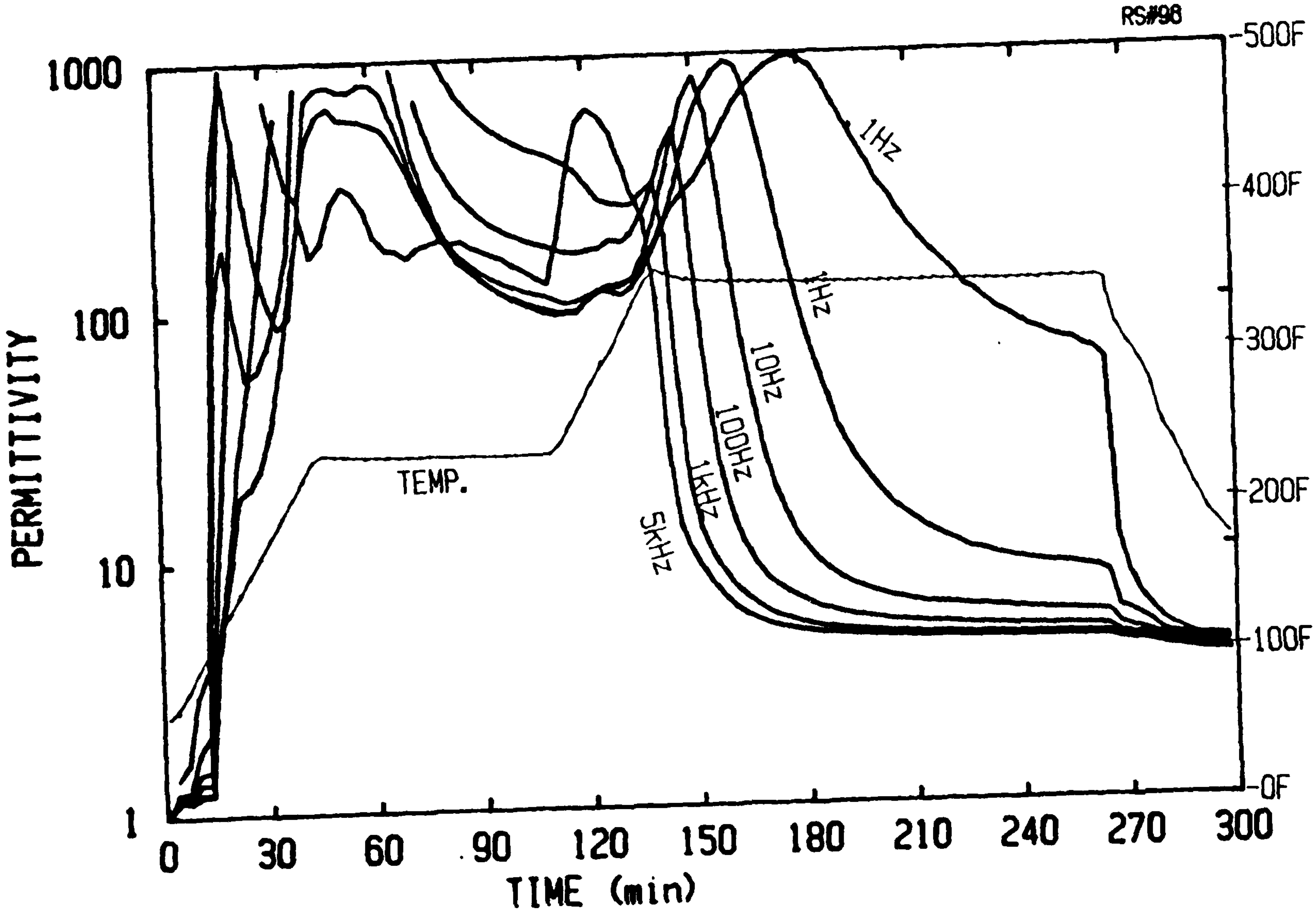
CURE OF 3501-6 RESIN IN OVEN
AUTOCLAVE CURE CYCLE

FIGURE 8



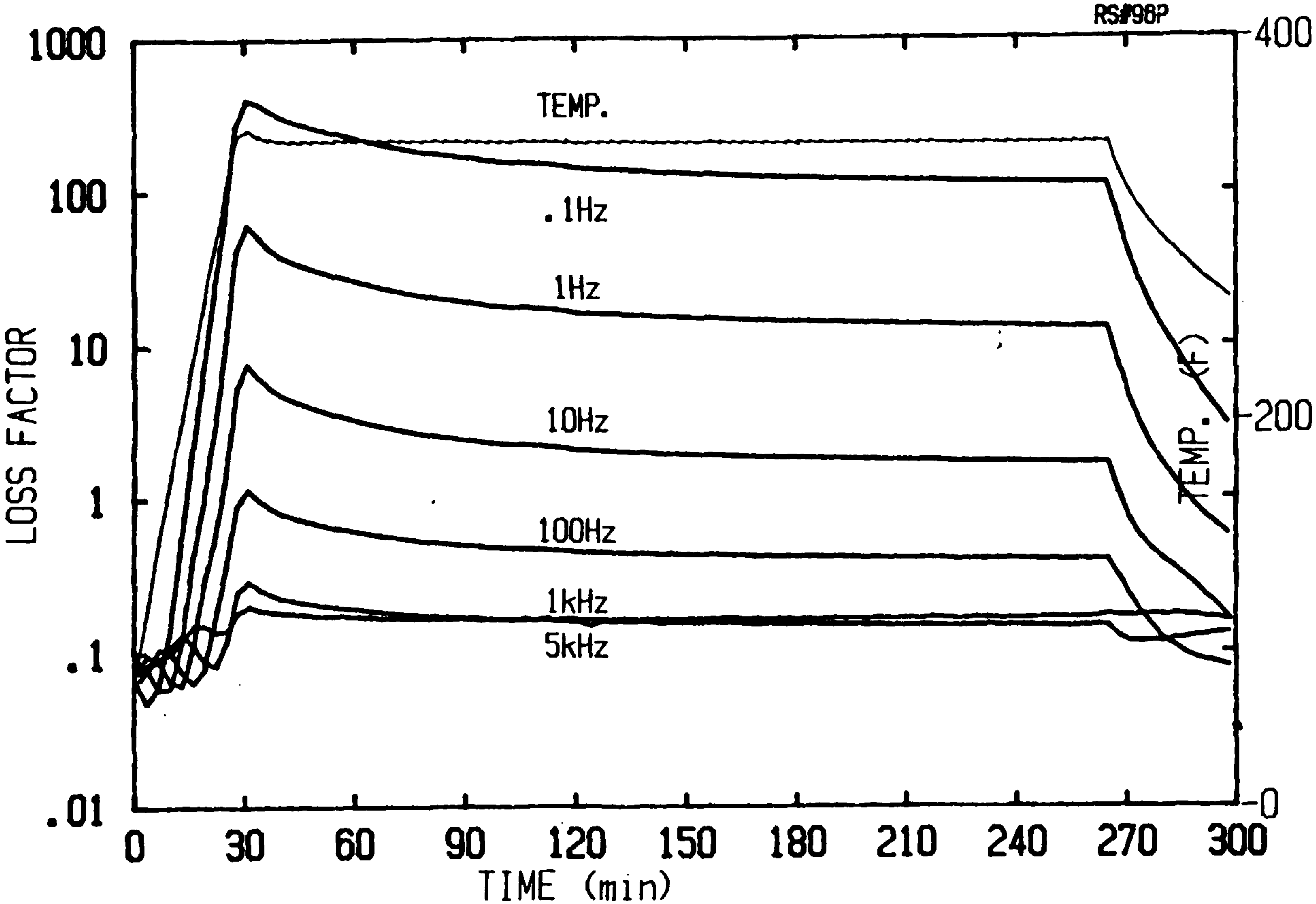
CURE OF 3501-6/AS4 CARBON EPOXY PREPREG IN PRESS
50 PSI AUTOCLAVE CURE CYCLE

FIGURE 9



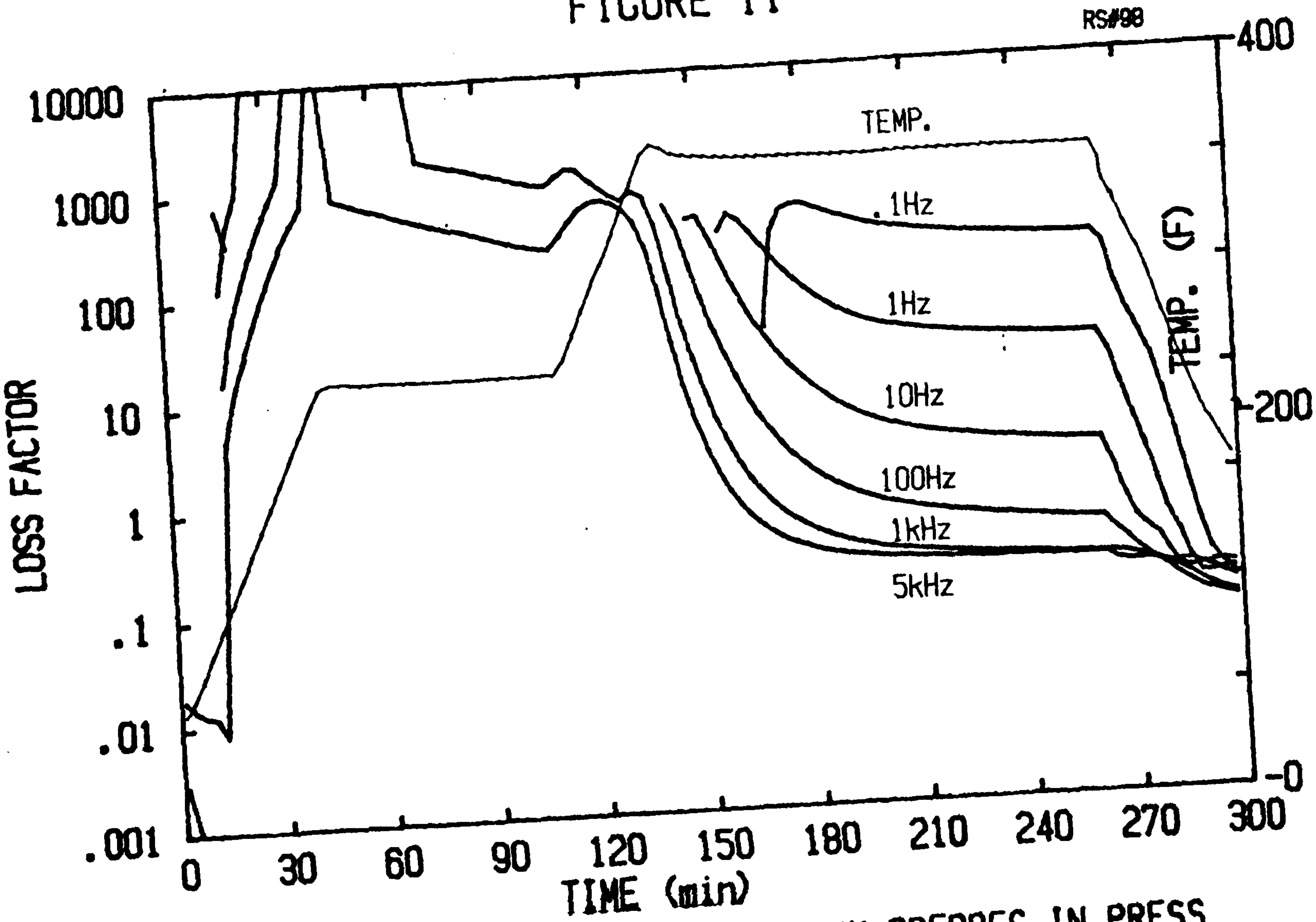
CURE OF 3501-6/AS4 CARBON/EPOXY PREPREG IN PRESS
50 PSI AUTOCLAVE CURE CYCLE

FIGURE 10



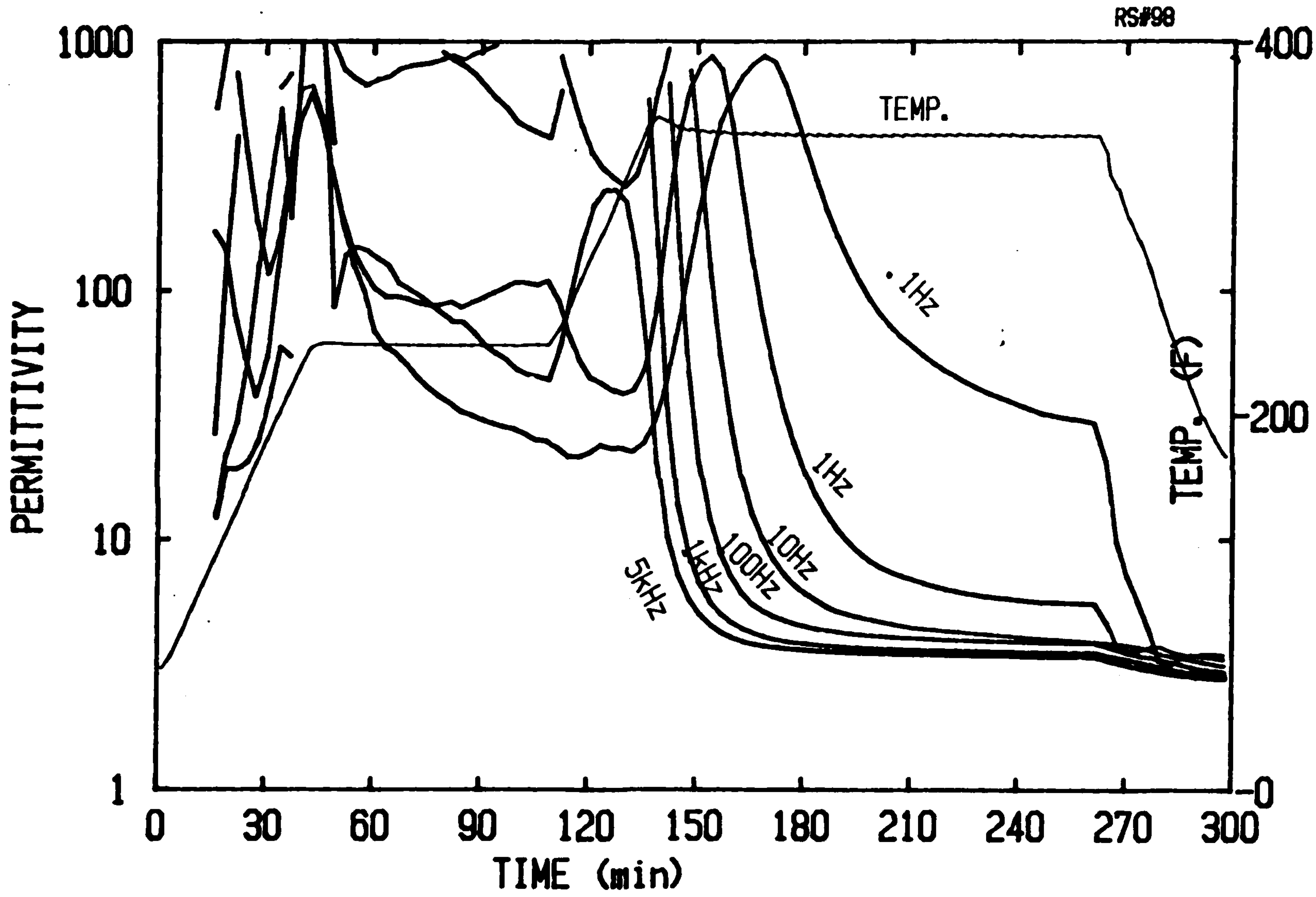
POST CURE OF 3501-6/AS4 CARBON EPOXY LAMINATE IN PRESS
4 HRS @ 350F

FIGURE 11



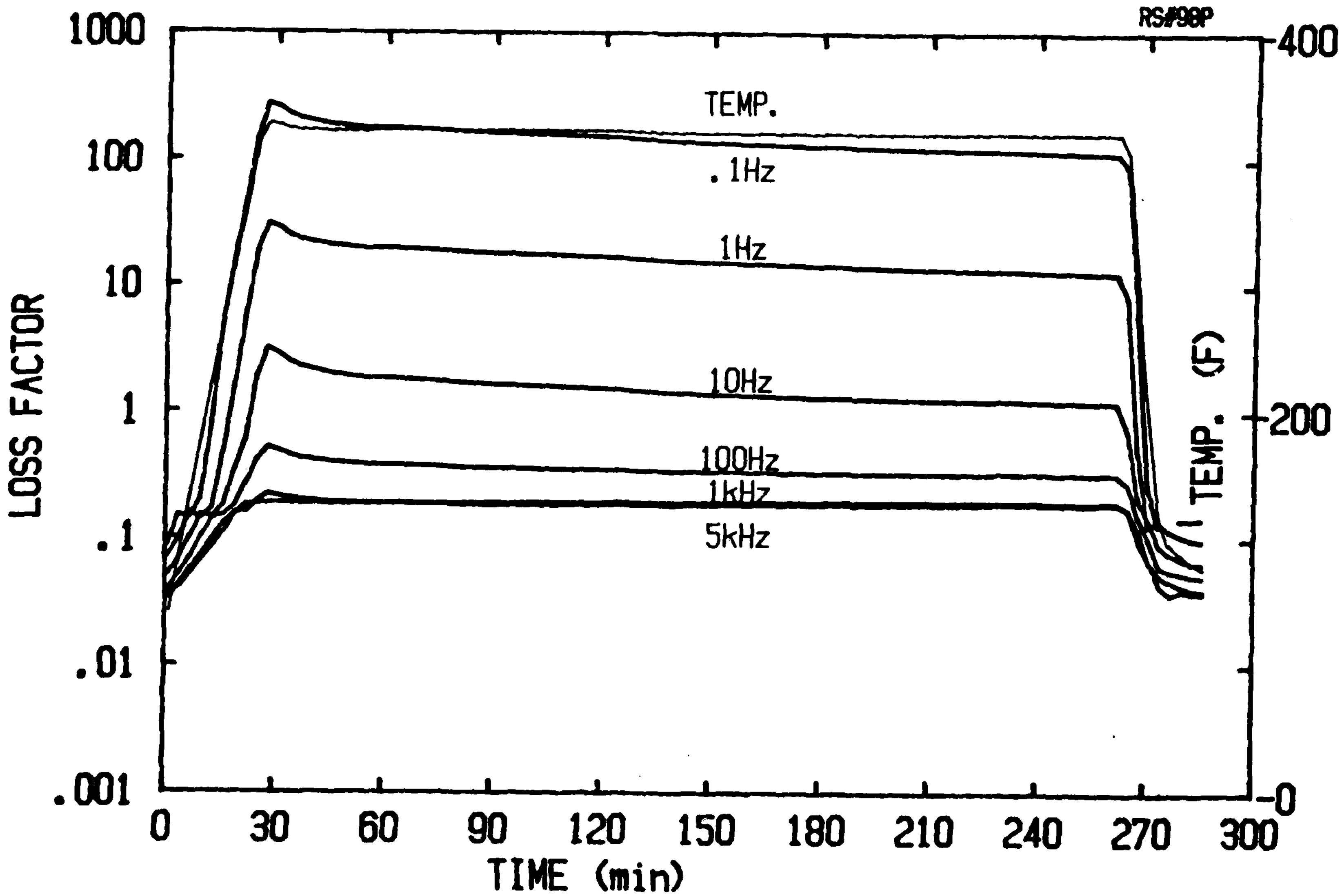
CURE OF 3501-6/AS4 CARBON EPOXY PREPREG IN PRESS
50 PSI AUTOCLAVE CURE CYCLE

FIGURE 12



CURE OF 3501-6/AS4 CARBON EPOXY PREPREG IN PRESS
50 PSI AUTOCLAVE CURE CYCLE

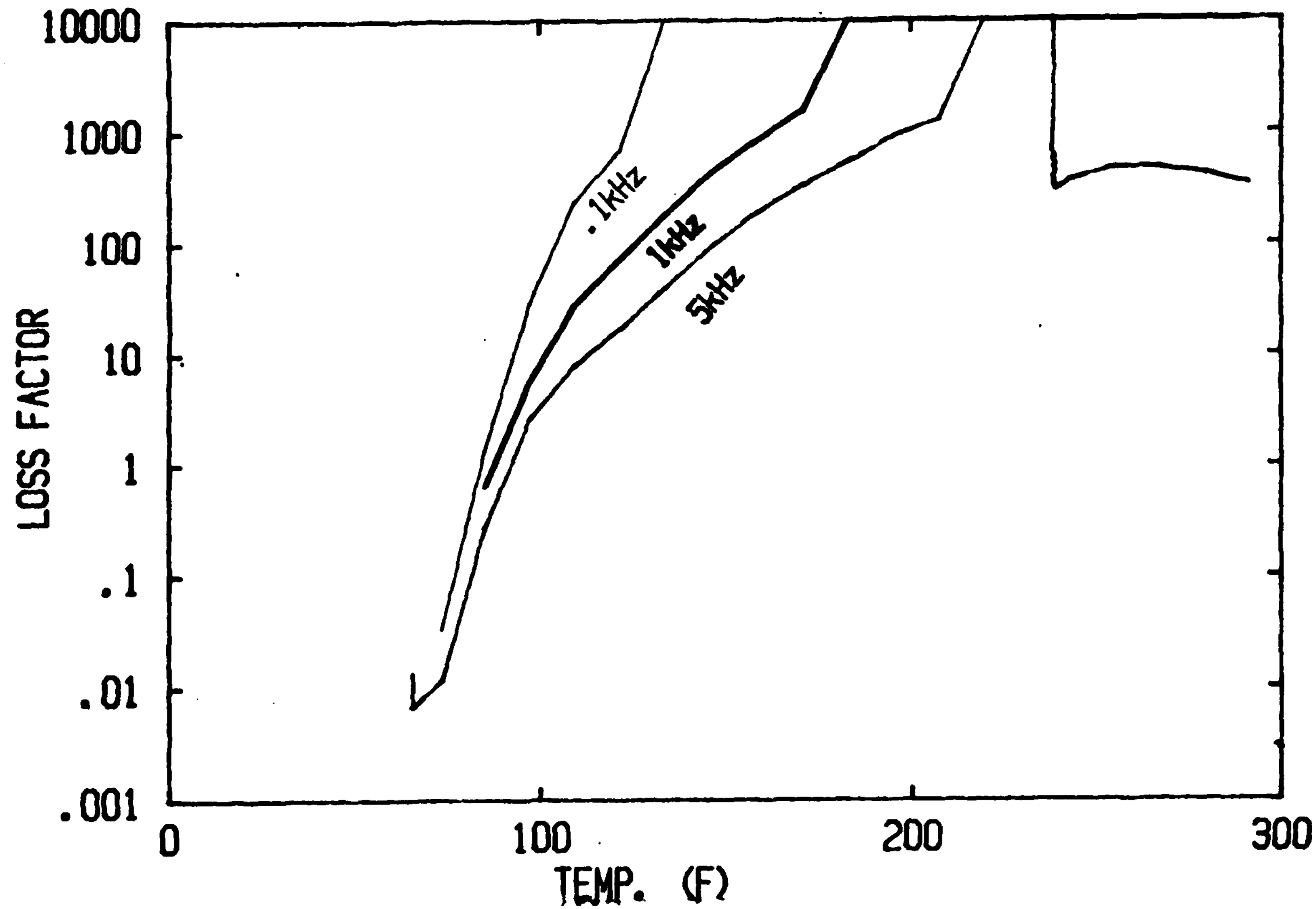
FIGURE 13



POST CURE OF 3501-6 GRAPHITE LAMINATE IN PRESS

50 PSI 4HRS @ 350F

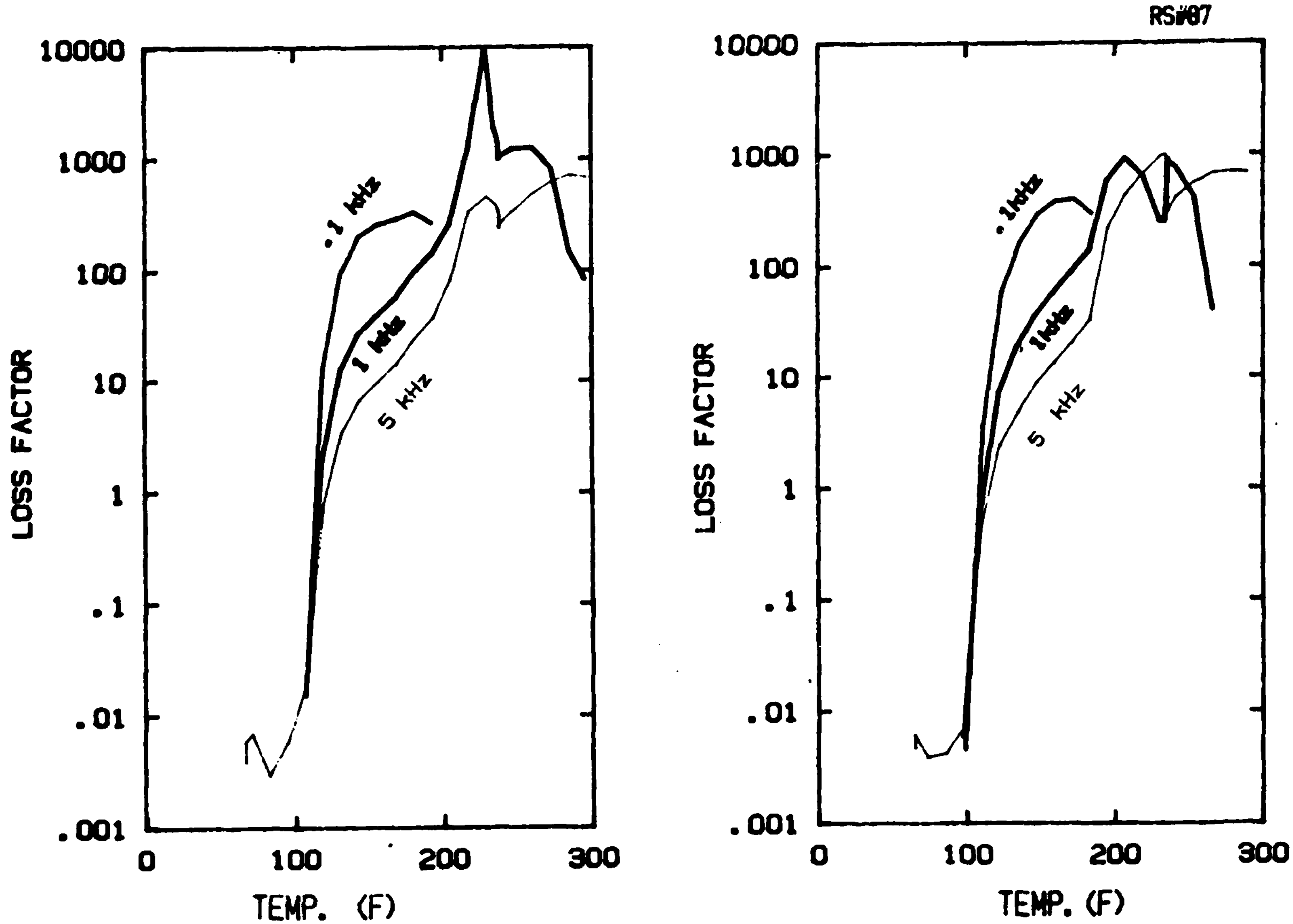
FIGURE 14



3501-6/AS4 CARBON EPOXY PREPREG IN PRESS

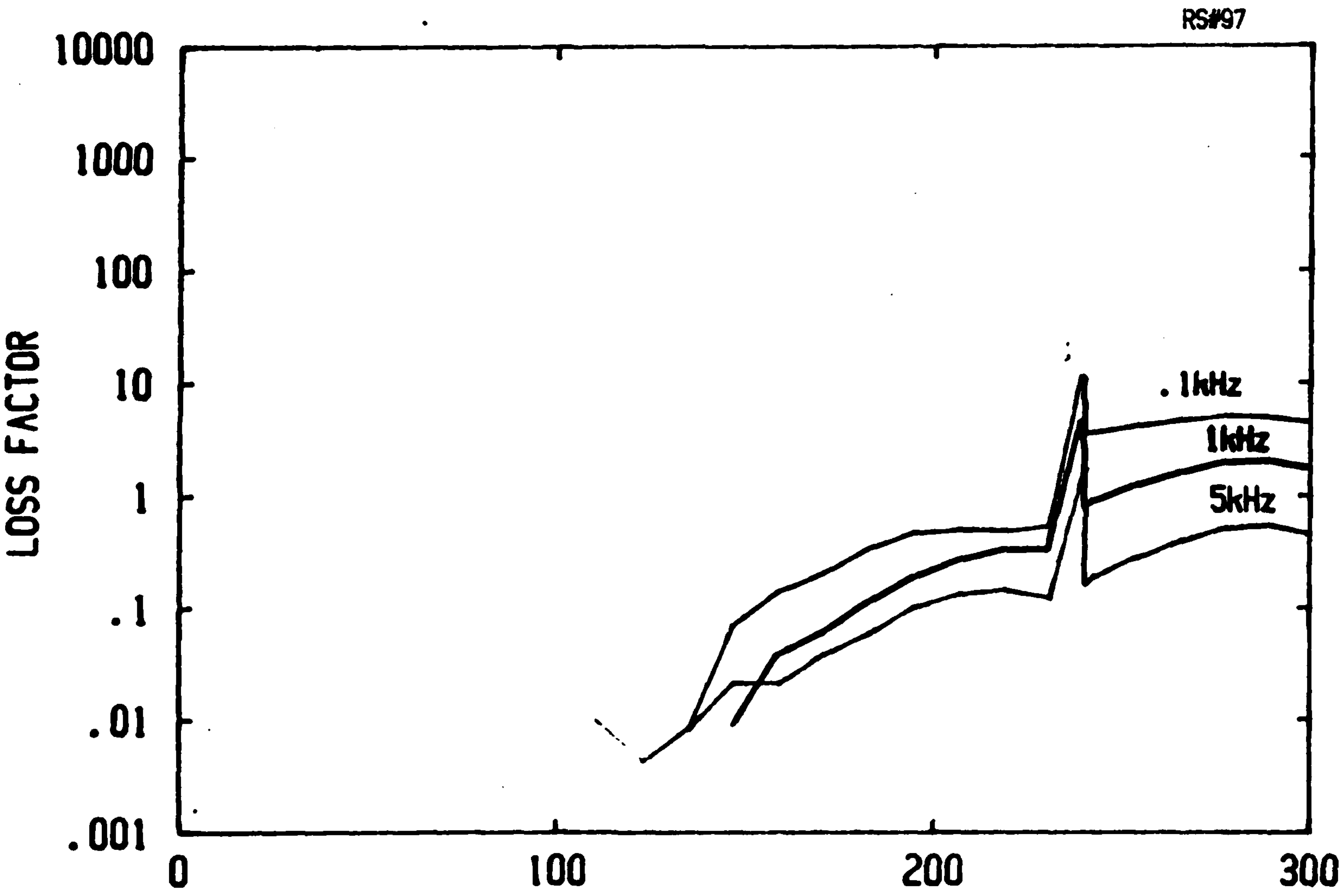
UNAGED PREPREG

FIGURE 15



3501-6/AS4 CARBON EPOXY PREPREG IN PRESS
PREPREG AGED 3 DAYS @ 90F & 90% R.H.
DUPLICATE RUNS SHOW GOOD REPEATABILITY

FIGURE 16



3501-6/AS4 CARBOR EPOXY PREPREG IN PRESS
PREPREG AGED 6 DAYS AT 90F & 90%R.H.

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